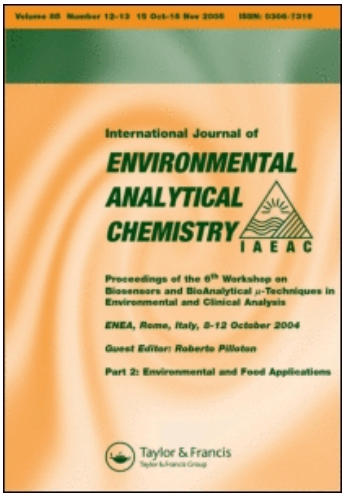

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Determination and Speciation of Mercury in a Dental Work-Place by Cold Vapour Atomic Absorption Spectrometry and Gas-Liquid Chromatography

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Cold Vapour Atomic Absorption Spectrometry (CVAAS) and Gas-Liquid Chromatography (GLC) have been used for determination and speciation of mercury. Total mercury, methylmercury, ethylmercury and phenylmercury concentrations in urine samples taken from students and staff of a dental work-place were investigated. Air samples were also analyzed. Detection limits, as three times the standard deviation, and in units of ng analyte per ml urine were found to be 1.7, 12, 2.4 and 21 for total mercury, methylmercury chloride, ethylmercury chloride and phenylmercury chloride, respectively.

KEY WORDS: Mercury speciation, gas-liquid chromatography, cold vapour atomic absorption spectrometry, dental mercury toxication.

INTRODUCTION

It is well known that many mercury compounds are very beneficial and thus have been used widely for industrial and medical purposes. However, toxic effects of mercury compounds on human are also

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well established and have been studied widely for a number of years.[1] Toxicity of mercury depends on both its concentration and chemical form. Alkyl mercury compounds are more toxic than aryl or inorganic mercury compounds.[2] The chemical form affects the degree of absorption, bio-transformation, retention and excretion modes. It has been estimated that more than 70% of methylmercury chloride ingested is eventually absorbed by human body, in contrast to only a figure of 5% for $HgCl_2$.[3] Regarding elemental mercury, its toxicity is greatly increased when in gaseous form. Inhalation of air contaminated with mercury vapour may result in intoxication and may be more harmful to the body compared to other means of entry, such as ingestion. Elemental mercury in gaseous form is lipid soluble and thus efficiently absorbed by lungs and enters the blood stream. [4, 5] Berlin and Johansson have reported[6] some data which suggest the absorption via respiratory track leads to higher rate of accumulation of mercury in brain than via other routes of absorption. Similarly, it has been shown that some organic mercurials are retained in the blood for longer periods, penetrate blood cell barriers, and become more firmly bound to tissues than inorganic mercury compounds.[7]

Regarding the analytical methods, as the sophistication in analytical instrumentation matured to higher levels and since the speciation, as well as determination of toxic elements became more important, a considerable increase of interest in these fields took place. Studies on mercury, one of the most important toxicants, allowed practical analyses to be carried out routinely at levels of $ng\,ml^{-1}$ for concentrations and ng for absolute amounts. Cold Vapour Atomic Absorption Spectrometry (CVAAS) has become a standard method for total mercury determination. CVAAS was first proposed by Poluektov and Vitkun[8, 9] and became well known after the commonly cited publication of Hatch and Ott.[10] A comprehensive review providing the historical and initial studies on CVAAS has been made.[11] Recently, by using amalgamation for preconcentration, determination of mercury at levels as low as $1\,ng\,l^{-1}$ has been reported by Welz *et al.*[12] A partial speciation as inorganic and organic mercury by CVAAS has been the subject of several studies.[13–15] A selective prereduction technique by using sodium borohydride for total and stannous chloride for inorganic mercury has been developed by Oda and Ingle.[16]

Detailed speciation of organomercury species such as methylmercury chloride (MMC), ethylmercury chloride (EMC) and phenylmercury chloride (PMC), however, requires employment of chromatographic methods. Several workers have performed separation of organomercury species prior to detection using the principles of electron-capture,[17] plasma emission spectrometry[18] or AAS.[19] Westöö[20–22] proposed a practical procedure for determination of methylmercury in fish and foodstuffs by GLC with electron capture detection; Schafer *et al.*[23] has later modified this method to apply for a wider range of biological samples. For determination of methylmercury in fish tissue, an alternative method was reported by Uthe *et al.*[24]

Among the kinds of places at which mercury intoxication is a hazard, dental work-places should be mentioned. Dental work-place personnel are subjected to mercury intoxication usually in the form of vapour which is caused by the presence of mercury used in amalgams. Several studies have shown that relatively high mercury levels were obtained both in working atmosphere and urinary samples from personnel working in this atmosphere.[25–27] Threshold limit value (TLV) for mercury in air has been given[27] as $0.05\,mgm^{-3}$, where in urine levels up to $0.015\,mgl^{-1}$ (15 ng/ml) are considered to be normal.[27]

In this study CVAAS and GLC have been used in order to optimize analytical methods which can be routinely used for determination of mercury in air and determination and detailed speciation in urine samples. A dental work-place has been selected as sampling medium. Since the source of mercury in the atmosphere of work-place is inorganic, speciation studies in air samples were not pursued. Speciation of organomercury compounds as MMC, EMC and PMC will be given, as well as total mercury content.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 305-B AA spectrometer with D_2 arc background correction system was employed. The absorption cell which was shaped according to the source light profile as in CVAAS system described before,[28] and a Perkin-Elmer mercury hollow

cathode lamp as source were used. Carrier gas, air, was provided by an ITT air compressor, regulated by AA spectrometer's conventional accessories and a second Duyer flowmeter. Signals were recorded by a Perkin-Elmer Model 056 strip chart recorder.

A Packard 7400 gas–liquid chromatograph was used for mercury speciation, with a Ni-63 EC detector. Carrier gas, N_2, was passed through a Packard gas filter cartridge having silica gel and molecular sieve. Glass columns were used with three different column materials; namely, 2.5% Carbowax 20M on 80–100 mesh Chromosorb W; 15% ethylene glycol adipate on 60–80 mesh Chromosorb W; and 1.5% OV-17+1.95% QF-1 on 80–100 mesh Chromosorb W-AW DMCS treated.

For all the columns described above column length was 195 cm and internal diameter was 0.2 cm. A Honeywell Elektronik 194 lab recorder was used to obtain the chromatograms.

Personnel Dust Sampler, Casella T 13020 was used for collection of air samples. Digestions were made in Parr Digestion Bombs, Model 4745. Adjustable Finnpipettes were used for preparation and diluted to 1.0 l with water. Solution was stored in dark.
borosilicate glass.

Reagents

All the reagents used were of analytical reagent grade. Triple distilled water was used.

Absorption solution for air sampling: 4.0 ml of 6% (m/V) $KMnO_4$ were mixed with 40.0 ml of dilute H_2SO_4 (1+1) and the mixture was diluted to 1.0 l with water. Solution was stored in dark.

10% (m/V) stannous chloride solution: 12.0 g of $SnCl_2.2H_2O$ was weighed into a 100 ml flask, dissolved by 18 ml of dilute HCl (1+1), and diluted to the mark. The solution was aerated at 1.0 l min^{-1} for 2 hours to remove the traces of mercury.

Mercury standard solution: All the solutions prepared containd 1000 mg Hg per litre. Appropriate amounts of $HgCl_2$ in water, and CH_3HgCl, C_2H_5HgCl and C_6H_5HgCl in benzene, were dissolved. Organomercury standards in methanol were similarly prepared. Intermediate standards and calibration standards were prepared daily.

Acidic NaBr solution: 77.5 g of NaBr were dissolved in 55 ml of dilute H_2SO_4 (1 + 1) and mixture was diluted to 250 ml with water.

Ethanolic $Na_2S_2O_3$ solution: 50 ml of 0.005 M $Na_2S_2O_3$ were mixed with 50 ml of 99.9% (v/v) ethanol in a 100 ml flask.

Procedures

Cleaning of glassware: Glassware used in CVAAS analyses were first placed in concentrated HNO_3 overnight, then rinsed 10 times with tap water and 5 times with triple distilled water. Glassware for GLC analyses were initially rinsed with chromic acid solution, then rinsed 10 times with tap water and 5 times with triple distilled water.

Preparation of air samples: Ambient air was bubbled at a rate of 2 l min^{-1}, through a 20.0 ml absorption solution in a gas washing vessel for 8 hours, using Personnel Dust Sampler Casella T 13020. Resulting solution was transferred into plastic bottles and kept in refrigerator, prior to analysis by CVAAS.

Pretreatment of urine samples for CVAAS: 1.0 ml of urine and 3.0 ml of concentrated HNO_3 were put into the teflon beaker of digestion bomb. The bomb was heated in an oven at 140° for 90 min. The bomb was cooled to room temperature, and the contents were transferred to a 50.0 ml volumetric flask and diluted to volume with water.

Pretreatment of urine samples for GLC: Procedure for this part is essentially as suggested by Uthe *et al.*[24] for fish tissue samples. 2.0 ml of urine were placed in a glass extraction vessel with ground joint stopper and in a shape suitable for centrifuging. 10.0 ml of 0.1 M $CuSO_4$, 5.0 ml of acidic NaBr solution and 10.0 ml of toluene were added, and the contents were shaken for 2 minutes. Then, the mixture was centrifuged for 10 minutes at 5000 min^{-1}. 8.0 ml of the upper (organic) phase was transferred into another extraction vessel of shape similar to the previous one. 1.0 ml of ethanolic $Na_2S_2O_3$ solution was added, and contents were mixed by hand vigorously for 10 s. The contents were centrifuged for another 5 minutes at 5000 min^{-1}. Ethanolic (lower) phase was transferred into another extraction vessel. Remaining toluene layer was re-extracted with 1.0 ml of ethanolic $Na_2S_2O_3$ solution. 1.0 ml of accurately measured

benzene and 0.5 ml of 3 M KI solution were added onto pooled ethanolic phases, and mixed for 10 s by hand. Then, the contents were centrifuged for 5 minutes at 5000 min^{-1}. 1.0 μl of benzene (upper) layer was injected into gas-liquid chromatograph.

Determination of total mercury by CVAAS: 5.0 ml of sample, either prepared by air or pretreated from urine, was placed in reduction vessel, 0.4 ml of 10% (m/V) stannous chloride was added, contents were mixed by a magnetic stirrer for 90 s. An air flow of 1000 ml min^{-1} was employed to carry the mercury vapour into the absorption cell, and the transient signal was recorded. Mercury was determined at 253.7 nm, with a spectral bandwidth of 0.7 nm, where hollow cathode lamp was operated at 6 mA. Typically, standard solutions containing 2–100 ng Hg were used for calibration. Aqueous standards were used for urine analyses, where absorption solution for air sampling was properly spiked with standard solutions to be used for calibration.

Determination of MMC, EMC and PMC by GLC: After the pretreatment of urine samples, 1 μl of final benzene phase was injected into column. Flow rate of N_2 was kept at its optimized value, 50 ml min^{-1}. Ni-63 ECD was operated at 5 V, with a sensitivity of 1×10^{-11} A and a suppression current of 1×10^{-8} A. Inlet and detector temperatures were 170°C and 240°C, respectively. Temperature program was used, with an initial step of 110°C and 6 min hold, rate of 15°C min^{-1} and finally a hold of 20 min at 220°C. Daily prepared and extracted standards in urine matrix were used for accurate calibration. In case of MMC and EMC, sharp peaks obtained allowed the use of peak heights instead of peak area. For PMC, however, a rather broad peak was obtained. When the precisions of measurements by peak area and peak height were compared by F test, no significant difference was observed in favour of the former. Therefore, peak heights, properly corrected by baseline method were used for calibrations.

RESULTS AND DISCUSSIONS

Digestion of urine samples

Urine samples were digested prior to determination of total mercury

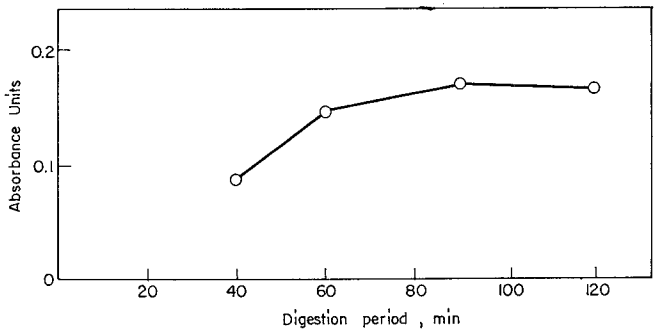

FIGURE 1 Change in peak height with digestion period for a urine sample.

by CVAAS, in order to eliminate matrix interferences. Digestion period at 140°C was optimized in order to assure complete release of mercury from the urine matrix. Figure 1 describes this optimization process for a urine sample. 90 minutes as a standard period of digestion for all the analyses were thus adopted. Longer periods would not be economical on time where shorter periods would result in negative errors.

Performance of CVAAS system

Daily calibrations were made for both air and urine samples. Slopes of the calibration line showed slight daily variations due to re-positioning of the absorption cell because of the fact that AA spectrometer was in use with other types of atomizers between periodic CVAAS analyses. Variations in slopes, however, were in the range of $\pm 10\%$. Average characteristic mass, m_0 was 0.9 ng Hg for 1% absorption. The detection limit was determined as the concentration equivalent of three times the standard deviation of 10 signals near the detection limit. Absolute and concentration detection limits were, 0.17 ng Hg and 0.033 ng Hg ml^{-1}, respectively. When the digestion procedure is taken into consideration, the detection limit for urine is 1.7 ng ml^{-1}. The best line was determined by linear regression method. The dynamic range approached up to 100 ng Hg. Correlation coefficients, R values, for 10 daily calibrations had a range of 0.9866–0.9999 with an average value of 0.9983.

Optimization of conditions and performance of GLC

Initially a glass column having 2.5% Carbowax 20M on 80–100 mesh Chromosorb W was used. This column, after several trials, was found to be unsatisfactory for resolution of MMC, EMC and PMC. Another glass column was tried, having 15% ethylene glycol adipate on 60–80 mesh Chromosorb W. This second column also did not provide the required analytical performance for chromatograms of organomercuries. Finally, a glass column was employed with 1.5% OV-17 plus 1.95% QF-1 on 80–100 mesh Chromosorb W-AW DMCS treated. The performance of this column was found to be satisfactory for the purpose and it was employed throughout the speciation analyses of organomercury compounds. A typical chromatogram of a mixed standard of organomercuries is given in Figure 2. The retention times for MMC, EMC and PMC were 3.0, 5.5 and 32.5 minutes respectively as can be seen from Figure 2.

The calibration plots resulted in at least two linear regions for organomercury compounds. Figures 3, 4 and 5 give the calibration plots for MMC, EMC and PMC, respectively. Initial portions of these plots, which correspond to lowest concentrations, were commonly employed. The detection limits were calculated in a manner similar to those for CVAAS in this study. The detection limits in units of ng analyte per ml, were found to be 12, 2.4, and 21 for MMC, EMC and PMC, respectively.

In order to improve the performance of OV-17 + QF-1 column, an occasional conditioning procedure was applied. For this, the column was initially conditioned for 48 hours, at inlet temperature of 200°C and column oven at 220°C, without connecting column to ECD. Then, 10 μl of 3.0 M KI was injected to the column, and kept for 1 hour under these conditions while N_2 has the usual flow rate of 50 ml min^{-1}. The adverse effects of contaminations by sample solutions and other impurities can be eliminated by this method which is originally used by Westöö.[21] This procedure was applied whenever the column performance significantly deviated from its usual quality. At the end of this process typical increases in sensitivity were 3 and 6 times for MMC and EMC, respectively, where the sensitivity for PMC decreased by about 25%.

After usual overnight heating period of the instrument, ECD had always high responses for first injection, since the organomercury

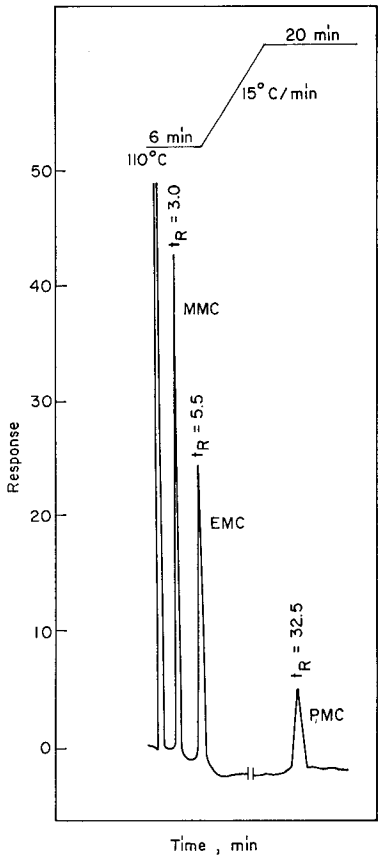

FIGURE 2 A chromatogram of mixture having 500 ng Hg ml^{-1} of each of MMC, EMC and PMC in benzene.

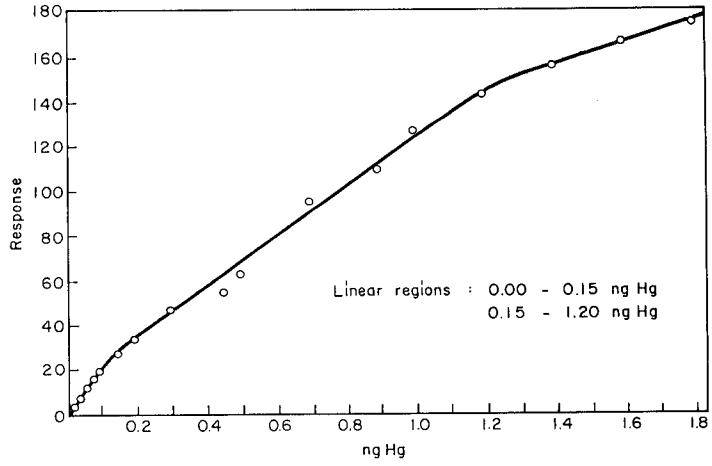

FIGURE 3 Calibration plot for MMC by GLC.

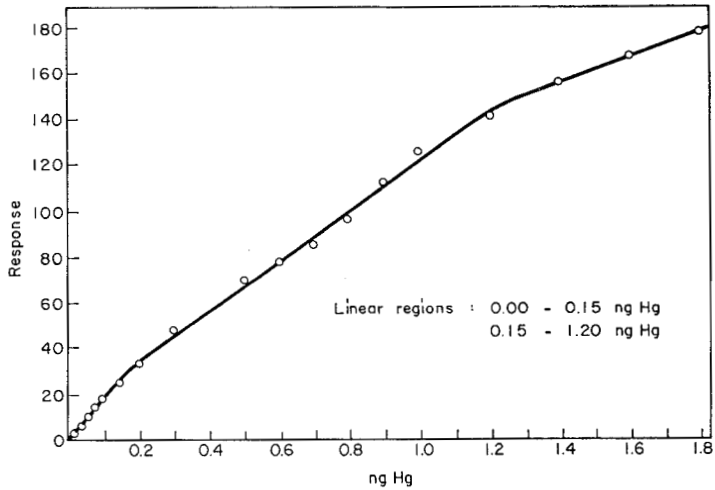

FIGURE 4 Calibration plot for EMC by GLC.

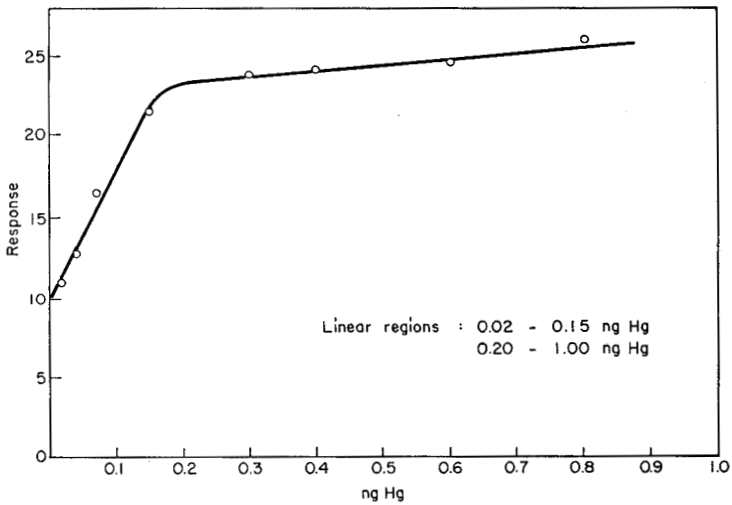

FIGURE 5 Calibration plot for PMC by GLC.

saturation in the system is somewhat cleaned during overnight heating. The proper detector and column conditions for the injec-

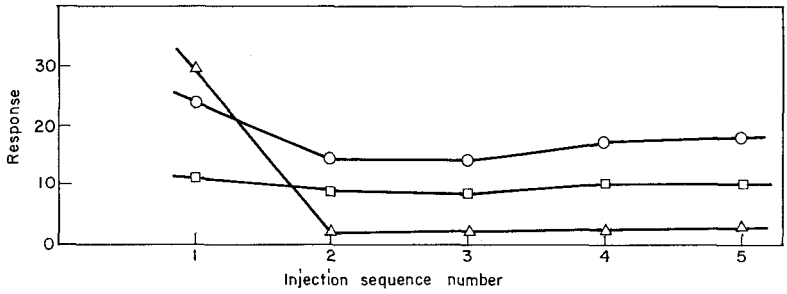

FIGURE 6 Optimization of Starting Time for GLC Speciation Analysis. 1 μl of mixture having 350, 500 and 250 ng Hg ml^{-1} was injected. 10 minutes were allowed between the runs. ○, MMC; □, EMC; △, PMC.

tions were optimized by using a mixture containing 350, 500 and 250 ng Hg ml^{-1} of MMC, EMC and PMC, respectively. An interval of 10 minutes was allowed between each run by 1.0 μl injections of this mixture. As can be seen from Figure 6, the system acquires a constant response after the fourth one in this series of injections. This is the appropriate time to begin the analysis, the injections afterwards should be performed continuously and periodically, allowing a waiting period of 10 minutes between the runs. For analysis of real samples the injections typically had relative standard deviation (RSD) values ranging between 2–12%, mostly around 5%. Since this level of precision was sufficient for the purpose in this study, the employment of an internal standard was not considered.

Results for samples from a dental work-place

The urinary samples obtained from 26 donors at the Faculty of Dentistry, Hacettepe University, were analyzed according to the procedure given for total mercury content. Mean value and mean deviation were 38.5 and 18.4 ng Hg ml^{-1} respectively, for duplicate samples obtained from 8 last year students, with a range of 21.0–73.4 ng Hg ml^{-1}. All of these values exceed TLV of 15.0 ng Hg ml^{-1}. Table I gives the results for faculty members, preclinic students and dental laboratory technicians. Seven faculty members had urinary Hg values ranging from 2.7 to 104.9 with a mean of 36.5 ng Hg ml^{-1} at the beginning of the study.

TABLE I

Results from analysis of urine samples for total mercury. Mean value and mean deviation of two values.

Type of Donor	Sample no.	ng Hg ml^{-1} First analyses	ng Hg ml^{-1} After precautions
Faculty members	1	26.2±1.7	20.1±0.1
	2	4.4±0.1	9.2±0.1
	3	2.7±0.1	11.9±0.1
	4	104.9±4.8	15.1±0.1
	5	5.8±0.1	8.2±0.1
	6	53.5±2.3	18.4±1.0
	7	58.1±1.4	20.1±1.0
		Beginning of Semester	End of Semester
Preclinic students	27	9.2±0.1	46.0±2.0
	28	21.0±0.1	16.0±0.1
	29	20.0±1.8	40.0±3.6
	30	15.6±0.1	23.0±0.1
	31	12.7±0.1	190.0±7.9
	32	20.0±1.5	18.3±1.4
	33	4.5±0.1	2.6±0.1
	34	4.5±0.1	143.7±4.3
	35	27.2±0.1	10.2±0.1
		First Analysis	After precautions
Dental laboratory Technicians	23	17.8±2.0	12.8±1.4
	24	53.5±2.3	22.9±1.6

The precautions taken after these results can be summarized as follows: (i) additional means of ventilation were provided and operated during work-place studies; (ii) instead of dry brushing as used before, wet brushing was applied after the floor was covered with sulfur dust; (iii) general hygiene rules on personnel were enforced. After these precautions, a range of 8.2 to 20.1 ng Hg ml^{-1} and a mean of 14.7 ng Hg ml^{-1} were obtained for the same group of donors, indicating a significant change in positive direction for better

hygiene conditions. In the same process the median value is reduced from 26.2 to 15.1. Results from 9 preclinic students at the beginning of semester had a range of 4.5–27.2 and a mean of 15.0 ng Hg ml^{-1}. The same group at the end of the semester during which they prepared several amalgams, had a range of 2.6–190.0, and a mean of 54.4 ng Hg ml^{-1}. The change was again in the logical direction. It may seem that two extreme values, 190.0 and 143.7, are highly responsible for this increase. However, the median value also increases from 15.6 to 23.0; and the highest value, 190.0, could not be rejected by Q test at 90% confidence level. Dental laboratory technicians, on the other hand, did also show a decrease in urinary mercury values after precautions as mentioned above were taken. Although the number of data is rather insufficient to draw any conclusions, a more steady level of mercury is expected in personnel who continuously are involved in amalgamation operations in contrast to students.

Total mercury values from air analyses are given in Table II. As TLV is 0.050 mg Hg m^{-3}, exceeding of this value was observed in amalgam preparation room, during work. Levels in clinics were definitely better and improved even further after the first set of results were announced and the precautions were taken.

TABLE II

Results from analysis of air samples. Mean value and mean deviation of two values.

Sampling Site	mg Hg m^{-3}	
Amalgam preparation room	Under usual conditions	During amalgam preparation
	0.0174 ± 0.0002	0.101 ± 0.005
	0.0165 ± 0.0015	0.086 ± 0.001
Clinics	First analysis	After precautions
At breathing zone	0.0483 ± 0.0001	0.0035 ± 0.0006
	0.0340 ± 0.0002	0.0033 ± 0.0001
At floor area	0.0033 ± 0.0001	0.0013 ± 0.0001

For mercury speciation, 15 urine samples out of 26 were selected. The chromatograms for Samples 24 and 16 are given in Figures 7 and 8, respectively. Sample 24 contained only MMC and Sample 16 contained only EMC, out of the organomercuries studied. Eight

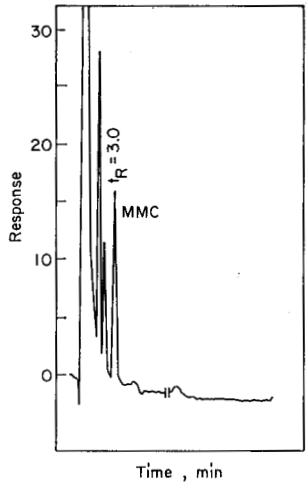

FIGURE 7 Chromatogram from 1.0 μl urine sample extract, No. 24.

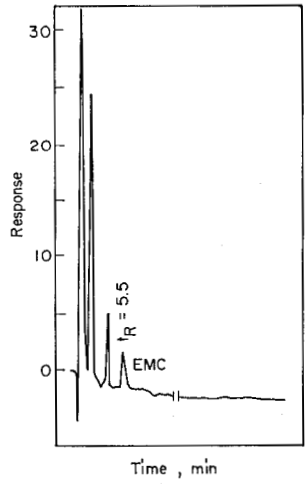

FIGURE 8 Chromatogram from 1.0 μl urine sample extract, No. 16.

samples out of selected 15 contained no detectable amount of any organic mercury species. Only in one sample EMC was present. PMC was below the detection limit in all cases listed in Table III. Percentage of mercury present as organic species ranges between 18.9 and 87.5. However, at present there is no evidence indicating whether the presence of organomercuries is due to body methylation from mercury vapour inhaled, or through direct ingestion of these species by daily diet.

TABLE III

Results from speciation analysis of urine samples. Mean value and mean deviation of two values, in ng Hg ml^{-1}.

Sample no.	Organic species			Total organic	Total	Organic % (m/m)
	MMC	EMC	PMC			
7	11.0±0.1	n.d.	n.d.	11.0±0.1	58.1±1.4	18.9±0.5
16	n.d.	26.0±0.1	n.d.	26.0±0.1	30.9±2.0	84.1±5.4
27	26.0±2.1	n.d.	n.d.	26.0±2.1	46.0±2.0	56.5±5.2
28	14.0±0.1	n.d.	n.d.	14.0±0.1	16.0±0.1	87.5±0.8
30	11.0±0.1	n.d.	n.d.	11.0±0.1	23.0±0.1	47.8±0.5
31	79.0±1.2	n.d.	n.d.	79.0±1.2	190.0±7.9	41.6±1.8
34	48.0±0.7	n.d.	n.d.	48.0±0.7	143.7±4.3	33.4±1.1

n.d. – Not detected.

CONCLUSIONS

Purpose of this work has been the assessment of the combination of two analytical techniques, namely CVAAS and GLC, for routine applications for mercury speciation in urine samples from workers of a dental work-place. A thorough investigation on the mercury hazards in such places is very necessary, not only to find the total mercury levels, but also to carefully speciate mercury compounds since the degree of toxicities are different. The analytical performance obtained by the techniques used here has been satisfactory, and certainly higher number of samples can be used from places larger than the one employed in this study.

It is useful to note that mercury levels in urine samples may not be considered as absolute indicators of exposure to this toxic

element; nevertheless, they can be useful on a group basis for a general evaluation of human exposure.[3] On the other hand, we believe that although the normal levels reported in literature are very useful, definition of normal levels in the region of study should be independently made; what is called as "normal value" may be dependent on local diet and environmental conditions for individuals who are to be used as control donors.

Consequently, data and procedures presented in this work are useful dor demonstrating that analytical techniques employed are proper for the purpose, as no serious complications have been observed and precision provided is sufficient. Regarding accuracy, however, lack of standards in their real matrices is a drawback for any work in this field. Well established and internationally recognized standard reference materials for MMC, EMC and PMC in urine are needed.

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